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SOME APPLICATIONS OF GALVANIC MANUFACTURE WASTE

In the work various directions of use of galvanic manufacture waste have been investigated. As a result of their analysis and experimental data the conclusion is drawn on impossible application of sewage deposits of galvanic manufacture as the additive for concrete mixes making due to their ecological danger. However, the given sewage deposits can be used in manufacture of a ceramic brick and colour glaze under condition of the obligatory ecological control of finished products. It is preferable to apply these deposits for colour glazed coverings as it is possible to substitute pigments by manufacture waste. It is also perspective to extract metals from sewage deposits of galvanic manufacture. Realization of the named directions will allow us to turn the given waste into valuable secondary raw materials, to expand an industry raw-material base, to lower negative influence on environment.

Introduction. Now in the Republic of Belarus about 30 million tones of production waste are formed, the level of their use remaining low – about 40% [1]. The greatest difficulty is represented by recycling dangerous waste such as waste of galvanic manufacture due to their complex chemical composition. The law of Belarus "On handling waste" sets up the priority of waste application to their neutralization or burial. Therefore the purpose of the given article is the search of the most rational directions of use of galvanic manufacture waste.

Main part. Depending on sources of formation and upon their prospective recycling technology galvanic manufacture waste can be divided into some kinds: spent concentrated technological solutions (electrolytes of coverings drawing, solutions of coverings removal, alkaline and acid etching solutions, etc.), washing waters, galvanic sludge, deposits of sewage.

Fig. 1 gives the most common methods of neutralization of galvanic manufacture waste.

It is clear, that methods of waste neutralization used in practice do not allow rational application of components which are present in them (nickel, chrome, copper, zinc, iron, etc.). Level of use of galvanic manufacture waste is still low, and the great bulk of waste is stored on the territory of the enterprises, very seldom it is stored outside of the enterprises. Though the volume of formation of galvanic manufacture waste at a number of enterprises does not exceed 10 t/year, the enterprises are compelled to store waste for many years on their territory due to absence of systems of waste neutralization.

The problem of neutralization and use of galvanic manufacture waste is complicated by a number of such factors as:

– variety of compositions of formed sludge and deposits of sewage;

– considerable fluctuations of a chemical composition of waste even within one enterprise in time period;

– heterogeneity of sludge on a consistency (from liquid suspension to a paste like state);

– presence of the substances (additives) which are a part of galvanic baths, etc.

This work considers in detail possible directions of use of sewage deposits of galvanic manufacture as nowadays this problem sharply faces the enterprises.

Now in most cases sewage deposits of galvanic manufacture after dehydration are stored on enterprise territory. Thus there appears not only a real threat of environmental contamination, but also such valuable scarce metals as chrome, nickel, copper, zinc, etc. are lost. Today in Belarus there are only three enterprises processing galvanic manufacture waste, – PPC "Silicate factory" (Bobruisk), Petrikov factory of expanded clay aggregate, PPC "Katpromstory" (settlement Kokhanovo, Vitebsk region). At the same time the literature analysis shows that sewage deposit of galvanic manufactures can successfully be used in various industries [2, 3]. Now there are following directions of their application:

1) extraction of metals from waste;
2) pigments obtaining;
3) obtaining of colour glaze coverings;
4) sorbents obtaining;
5) catalysts obtaining;
6) their usage as additives in an iron and steel industry;
7) concrete and asphalt concrete obtaining;
8) obtaining of building ceramic materials.

In most cases it is offered to use sewage deposits of galvanic manufacture in the industry of building materials for making concrete mixes, wall ceramic materials, fillers for light-weight concrete (expanded clay aggregate, aggloporite), face ceramic materials.

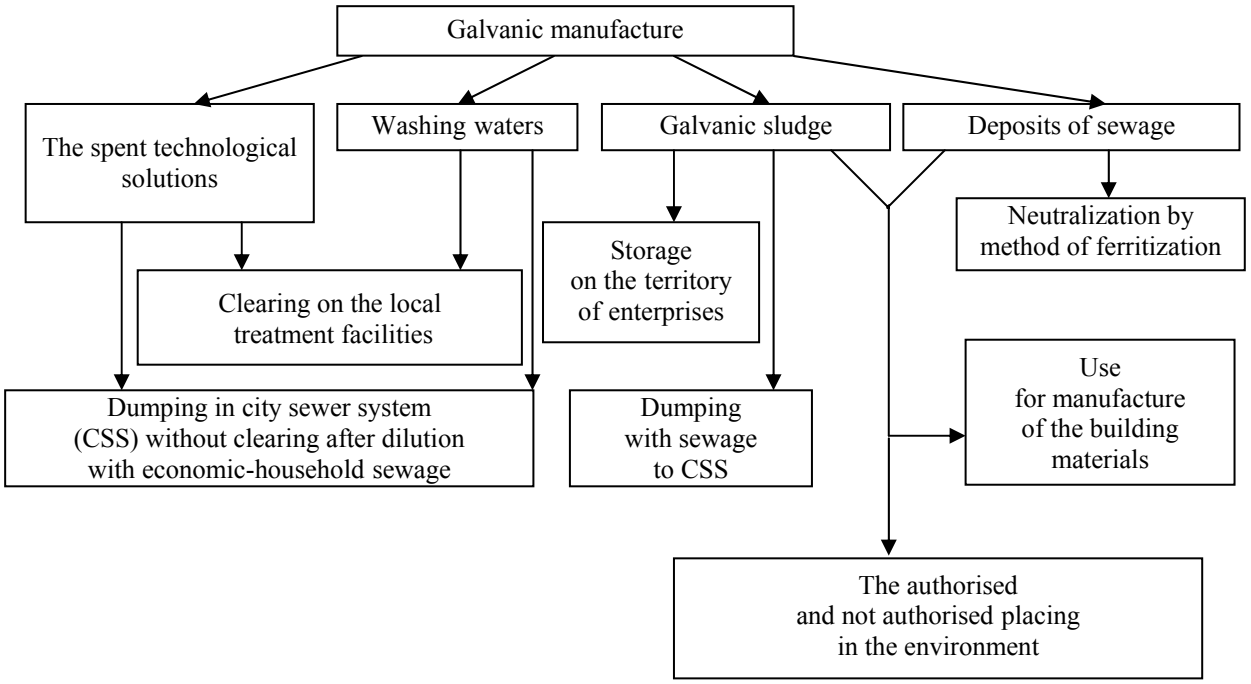

Fig. 1. Methods of neutralization of galvanic manufacture waste

The article presents the results of research for concrete making with the use of sewage deposit of galvanic manufacture containing chrome, copper and zink hydroxides at Borisov factory of plastic products (BFPP). Cement of grade 400, sand as an aggregate and water were applied to make a concrete mix. Predried and crushed deposit of sewage was added to a concrete mix in quantity from 5 to 20 wt % (In terms of a dry substance) instead of sand. Samples of the cubic form in the size of 10×10×10 cm have been made of the received concrete mixes. Samples hardened at a room temperature in 28 days.

Research of physical-mechanical properties (density and compressive strength) of the received samples has shown that they practically do not change in the mentioned range of concentration in comparison with the concrete mix received without using sewage deposit of galvanic manufacture BFPP. However, in this case there is a danger of washing away of heavy metals and pollution of the environment by them, first of all underground waters and soil. To determine danger of the received samples they were extracted in various environments (acid, alkaline and neutral) at 20°C in the ratio of sample : water – 1 : 10. Tests were selected every 30 days and analyzed for the presence of heavy metals by chemical methods of the analysis. In the acid environment (pH = 4.8) for the samples containing 10 wt % of an involved waste, there observed intensive washing away of ions of heavy metals (concentration Cu^{2+} – 0.5 mg/l, Zn^{2+} – 0.05 mg/l, Cr^{3+} – 0.02 mg/l), that testifies to impossibility of use of mentioned waste in concrete making in case of its contact with the given environment.

Introduction of sewage deposit of galvanic manufactures in quantity to 20 wt % (by a dry substance) for the production of rough ceramics and aggregates for light-weight concrete (e.g. expanded clay aggregate) is known to improve physical mechanical properties of ceramic materials [4–6].

In the given work clay from "Zapol'e" and the dehydrated sewage deposits of galvanic manufactures of various Belarusian enterprises were applied to make face ceramic brick. It is clear from the table, that in most cases the optimum quantity of deposit was 10–20 wt %. It can be caused by achievement (at the given content of sewage deposit) of the optimum chemical composition which provides a maximum quantity of melt formed at roasting.

To determine sample stability the above described technique was used. Ions of zinc, chrome and nickel in the received extracts have not been found out. The maximum content of ferric ions were observed at extracting the samples containing sewage deposit of galvanic manufacture of JSC "BelVar" in the acid environment (2.5 mg/l).

To research binding force of heavy metals in a brick extraction of the received samples containing 20 wt % of sewage deposit of galvanic manufacture of JSC "BelVar" was carried out in the most severe conditions, i.e. shattered at 100°C in various environments (acid, alkaline and neutral) during 8 h at ratio of solid and liquid phases 1 : 10. Tests were taken each hour and analyzed for the presence of heavy metals by atomic absorption method. Results of analyses taking into account basic concentrations are presented in Fig. 2–4.

Properties of samples of the face ceramic brick received with use of sewage deposits of galvanic manufacture

Deposit of sewage galvanic manufactures	The optimum content, wt %	Properties of samples		
		compressive strength σ, MPa	water absorption *W*, %	density ρ, kg/m^3
JSC "BelVar"	20	33	15.2	1,750
Joint-Stock Company "Atlant"	20	35	14.1	1,800
Minsk Motovelozavod	20	34	15.3	1,760
UE SCIA"Centre"	10	30	19.4	1,680
The Minsk motor factory	20	31	18.7	1,700
Factory "Electromodyl"	15	32	16.4	1,720
JSC "Borisov plastic products Plant"	20	35	14.3	1,790
Without waste	–	30	19.1	1,700

From schedules it is clear, that concentration of chrome and zinc ions in extracts even in the most severe conditions is very small (not more than 3.5 mkg/l), nickel ions have not been found out at all. Apparently, it is connected with transition of heavy metals in strong and almost insoluble compounds – silicates and alumina silicates – at high-temperature processing. Relatively higher concentrations of ions of iron are caused by its high content in initial raw materials: concentrations of Fe^{3+} after extraction of brick samples containing sewage deposit of galvanic manufacture, and without them practically do not differ (curves *1* and *3* on Fig. 4).

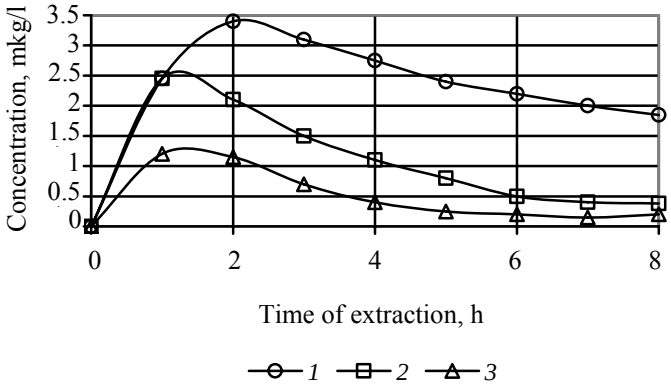

Fig. 2. Kinetics of Cr^{3+} extraction from a brick in various environments:
1 – brick with 20 wt % of a deposit of sewage of galvanic manufacture JSC "BelVar" (pH = 4);
2 – a brick with 20 wt % of a deposit of sewage Galvanic manufacture of JSC "BelVar" (pH = 7);
3 – a brick without a deposit (pH = 4)

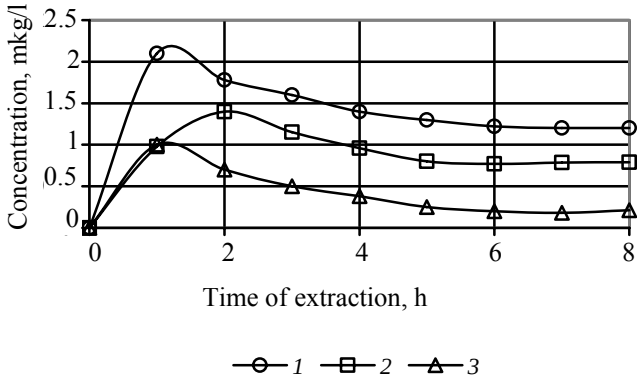

Fig. 3. Leaching kinetics Zn^{2+} from a brick in various environments:
1 – a brick with 20 wt % of a deposit of sewage of galvanic manufacture JSC "BelVar" (pH = 4);
2 – a brick with 20 wt % of a deposit of sewage Galvanic manufacture of JSC "BelVar" (pH = 7);
3 – a brick without a deposit (pH = 4)

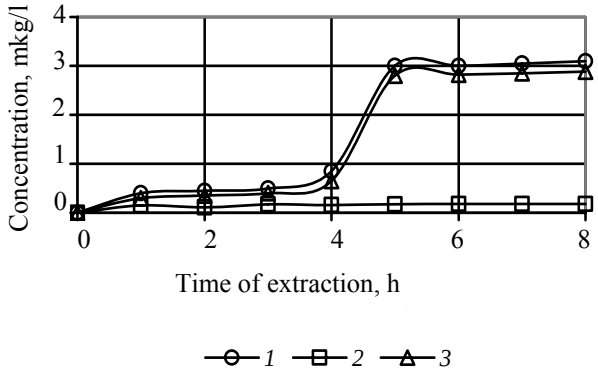

Fig. 4. Leaching kinetics Fe^{3+} from a brick in various environments:
1 – a brick with 20 wt % of a deposit of sewage of galvanic manufacture JSC "BelVar" (pH = 4);
2 – a brick with 20 wt % of a deposit of sewage Galvanic manufacture of JSC "BelVar" (pH = 10);
3 – a brick without a deposit (pH = 4)

However use of sewage deposits of galvanic manufactures for manufacturing ceramic materials is not the best decision as thus only small amounts of useful properties of the metals which are a part of a waste are realized, and possibility of their extraction and use as secondary raw materials is forever lost.

Now deposits of sewage of galvanic manufactures are also offered to be used for making colour glazes [7]. In the given work glaze coverings have been received on the basis of fritted glazes of JSC "Berezastroymaterials" with addition of predried up deposits of sewage of galvanic manufactures of the above-mentioned enterprises (Table), and also the Minsk factory of printed-circuit boards (MPCBF). The deposit of sewage was added in number of 10 wt % by a dry substance, glaze was put by a watering method, the roasting temperature was 1,000°C. High quality glaze coverings of various colours (brown, mustard, turquoise) depending on deposit composition (the content of painting ions of iron, chrome, copper etc.) have been received. Stability of glaze coverings to environment factors is also provided and it is proved by experimental data. In work ecological safety of the glaze received with addition of 10 wt % of sewage deposit of the galvanic manufacture at MPCBF containing hydroxide of copper was investigated. A solution of a washing-up liquid or acid solution (pH = 4) was poured into a ceramic cup with a given glaze covering. Extraction was carried out during 8 h at 100°C, tests for the presence of copper ions were analyzed by atomic absorption method. Concentration of copper ions in the acid environment is higher than in a washing-up liquid solution (2.4 and 1.6 mkg/l accordingly), however in both cases it is exceedingly low despite severe conditions of extraction.

Deposits of sewage of galvanic manufacture can also be used in manufacture of pigments since the majority of the heavy metals entering into their structure, possess chromophorous properties and are components of industrial ceramic pigments. With use of mentioned waste for manufacturing ceramic pigments one can solve not only an environmental problem, but also there appears a possibility to reduce or completely to exclude the consumption of expensive, scarce compounds of the heavy metals which are not produced in Belarus. It reduces the cost price of production of mineral pigments with black, brown and yellowy-brown colours [8].

One of the most perspective directions of processing of sewage deposits of galvanic manufacture is extraction from them the heavy metals which concentration frequently exceeds their quantity in natural ores. Pyrometallurgic and hydrometallurgic methods of metal production from considered waste are developed [9].

Among thermal (pyrometallurgic) technologies there is one more method of processing of the waste containing heavy nonferrous metals, namely by a reduction smelting with the subsequent rectification and separate obtaining metals in the form of commodity products. Nowadays, there are some new technologies assuming consecutive carrying out of the following stages: dehydration and drying of deposits, low temperature reductive processing with obtaining powdery metal concentrates, their melt for obtaining pure metals and alloys. The main drawback of the given technologies is high power consumption and a considerable quantity of secondary waste.

The essence of hydrometallurgical methods consists in extraction of metals from ores, concentrates and a waste at their processing by water solutions of chemical reagents with the subsequent isolation of metal or its chemical compound from a solution. The interesting scheme of processing of sewage of galvanic manufacture was offered by

employees of the Netherlands institute of applied natural-science researches and an institute of technology in Eindhoven [10]. According to the process developed by them, after leaching heavy metals iron is extractively isolated, and then chrome is oxidized to a six-valent state and as a result of interactions with lead ions the latter precipitate in the form of chromate.

If it is necessary to isolate manganese it is done by oxidation by bleaching liquor. Then the solution is alkalized and the chrome residua are removed with the help of anion exchange resin. Further copper and other nonferrous metals (cobalt, zinc, cadmium and nickel) are extracted by an extraction method in two stages. Division of the latter is carried out by methods of an ionic exchange and extraction.

The given technology allows practically all useful metals to be extracted individually from sewage deposit of galvanic manufacture. However it is reached by the big variety of used physical and chemical methods that complicates hardware registration of process and demands highly skilled service.

The authors of this article recommend to extract heavy metals from sewage deposits of galvanic manufacture in two stages: 1) to separate various sewage of the given manufacture; 2) to treat them and then extract metals from deposits formed.

Conclusion. The carried out analysis of directions of use of sewage deposits of galvanic manufacture testifies to possibility of application of considered waste as the additive for making ceramic bricks and colour glazes under condition of the obligatory ecological control of finished goods. The use of sewage deposit of galvanic manufacture for colour glaze coverings is preferable because of the replacement of expensive import pigments by a waste. Extraction of metals from deposits of sewage of galvanic manufacture is also considered to be perspective.

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